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(54) MANUFACTURE OF PURE ALKALI METAL SALTS OF AMINOPOLYCARBOXYLIC ACIDS

(71) We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESSELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved process for the manufacture of pure alkali metal salts of certain aminopolycarboxylic acids by reacting alkali metal cyanides with formaldehyde and, optionally, with appropriate polyamines in aqueous solution.

It is known that the reaction of alkali metal cyanides with formaldehyde in aqueous solution to form nitrilotriacetic acid salts and the reaction of alkali metal cyanides with formaldehyde and diamines or polyamines in aqueous solution of form other aminopolycarboxylic acid salts produce good yields.

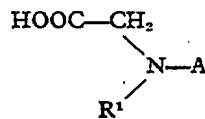
The proportion of by-products, as manifested by fairly pronounced discoloration of the product for example, is too high, however, being equal to up to 10% of the salts of aminopolycarboxylic acid obtained in this manner. There has been no lack of attempts to obtain a pure salt by concentrating the solution emerging from the reaction. However, it is not possible to utilize the solution to the full using this method, as it is well known that a precipitated salt becomes more and more impure the more the solution is concentrated. In the manufacture of salts of aminopolycarboxylic acids there is the added difficulty that such salts are very soluble in water and the viscosity of the mother liquor increases steeply.

However, it would be uneconomical if only a portion of the salt present in the solution were recovered, as the portion remaining in the mother liquor would be lost. Where it has been necessary to obtain the salt of an aminopolycarboxylic acid in solid form, it has been common practice to evaporate the solution emerging from the reaction to dryness or to treat it in a spray drying tower, in which case the impurities remain in the product.

For many purposes, however, a product of this degree of purity is inadequate.

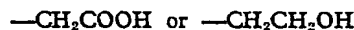
The present invention seeks to provide an improved method of producing pure alkali metal salts of aminopolycarboxylic acids, for example pure alkali metal salts of nitrilotriacetic acid, ethylenediaminetetra-acetic acid and hydroxyethylethylenediaminetriacetic acid.

According to the invention there is provided a process for the manufacture of a pure alkali metal salt of an aminopolycarboxylic acid of formula I:



I

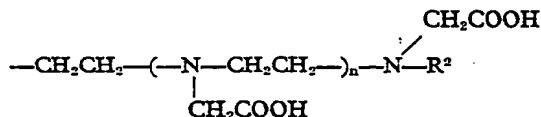
in which R^1 denotes a hydrogen or a group of the formula



and A denotes a group of the formula

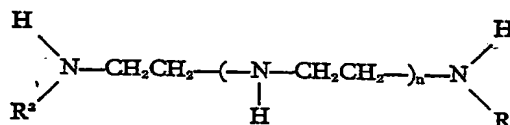


or a group of formula II:



II

metal cyanide, formaldehyde and, where A denotes a group of formula II, a compound of formula III:



III

Preferred starting materials are ethylene diamine and hydroxyethylethylene diamine. As mentioned above, in the preparation of alkali metal salts of nitrilotriacetic acid it is sufficient to use formaldehyde and the alkali metal cyanide in amounts such that an appropriate amount of ammonia is formed as intermediate according to the following equation:


$$3\text{NaCN} + 3\text{H}_2\text{O} + 3\text{CH}_2\text{O} \rightarrow \text{N}(\text{CH}_2\text{COONa})_3 + 2\text{NH}_3$$

The compounds in which A is a group of formula II may be prepared from the said polyamines, alkali metal cyanides (preferably sodium cyanide) and formaldehyde in known manner.

$$(A=R'=\text{CH}_2\text{COOH}).$$

The method of the invention may be readily applied to the said compounds and produce considerably purer products.

At first sight, the characteristic feature of the process of the invention appears to be very simple, but it is in fact a surprising and inventive measure that has hitherto been avoided for the following reasons:

It is well known that when a saturated solution is concentrated, the product dissolved therein precipitates whilst the impurities remain in the mother liquor. However, with increasing concentration of such solution, the impurities tend to adhere to the precipitated product to an increasing extent. In other words, evaporation of the solution has to be terminated at the point where the precipitated product is still substantially pure but is on the point of becoming impure. In the case of salts of the aforementioned aminopoly-carboxylic acids, a solution is obtained from the reaction of the aforementioned starting materials which, when evaporated to dryness, gives a product containing up to 10% of impurities, as mentioned above. One would have thought, therefore, that the impurities would accumulate in the reaction chamber if the concentrated mother liquor containing all of the impurities was combined with fresh reactants. From this it would follow that the solution obtained from the said reaction could only be evaporated to a slight extent as

otherwise the said impurities would be found in the solid product.

This is not the case in our new process, and the successful operation of the process on an industrial scale constitutes the removal of a definite prejudice in this field.

The method of carrying out the process without the measure of the invention is described in numerous patent specifications and essentially consists in causing aqueous alkali metal cyanide solutions, preferably sodium cyanide solutions, to react in a number of stages with formaldehyde and, where A denotes a group of formula II, with a diamine or polyamine of formula III. It is convenient to divide the process up into a number of reaction zones, the first zone being operated with an excess of amine and, if necessary, at elevated pressure. In the second stage, i.e. in the second reaction zone, a substantially quantitative conversion to the appropriate alkali metal salt of the aminopolycarboxylic acid in question generally takes place with, for example, removal of the ammonia formed (from sodium cyanide) as a by-product of the reaction (as may be effected by lowering the pressure for example) and with continued introduction of alkali metal cyanide and formaldehyde.

A last refinement of this process is a procedure in which the reaction is carried out in two cascade-connected reaction zones using stoichiometric amounts of the reactants, as is controlled by means of, say, a potentiometric measuring element, so that the concentration of alkali metal cyanide in the reaction mixture in the first reaction zone or zones is held at a substantially constant value selected with a view to keeping the alkali metal cyanide concentration in the final reaction zone down to less than 100 ppm and preferably down to a value as low as 10 ppm or less.

In this latter embodiment, the conversion rate achieved is substantially quantitative. Substantially 100% purity of the solid product is sought to be achieved by the process of the present invention.

The aqueous solutions of the alkali metal salts, preferably sodium salts, of aminopolycarboxylic acids produced by, say, the method described above may be subjected to the treatment of the invention either continuously or batchwise.

Batchwise operation of the present process is simple. The solution of the salt of the aminopolycarboxylic acid is evaporated, for example to an extent such that a portion, preferably about 50%, of the expected theoretical yield of salt separates out, and this precipitated salt is removed from the concentrated solution. Conventional methods such as filtration or centrifuging may be used. The concentrated solution is returned to the reaction chamber. Further quantities of said starting materials (alkali metal cyanide, formalde-

hyde and, where A is a group of formula II, a diamine or polyamine of formula III) are introduced which are then reacted. This produces another batch of reaction solution which is also subsequently subjected to the treatment of the invention, and so on.

In principle, batchwise operation of the process may be repeated as frequently as desired. However, it is convenient to remove part of the concentrated mother liquor after a few batches in order to keep the concentration of impurities below a specific limit. The amount of mother liquor which need be removed from the process is small, being not more than from 5 to 12% by weight of the mother liquor for example, on the basis of the removal of about 50% of the salt of the aminopolycarboxylic acid from the reaction solution. If larger or smaller proportions of said salt are removed, it will be necessary to remove appropriately larger or smaller proportions of mother liquor from the process.

In continuous operation, the solution of the salt of the aminopolycarboxylic acid passes to, say, a heated stirred vessel, where it is concentrated by evaporation until preferably half of the expected theoretical amount of solid salt has precipitated, this being separated from the liquid, for example on a suction filter. The moist salt is then washed with a little water and dried in the usual way to give a product having at least 98.5 to 99.5% of pure salt of the aminopolycarboxylic acid. The remaining concentrated mother liquor, which contains nearly all of the impurities as well as the remaining amount of salt, which is preferably equal to about 50% of the total salt, is continuously recycled to the reaction chamber, for example by means of a metering pump, together with the requisite starting materials (formaldehyde, alkali metal cyanide solution and, if necessary, diamine or polyamine). Metering of the mother liquor and the rate of feed of the starting materials are adjusted so as to achieve a steady state in the circulatory process, i.e. constant reaction conditions in the reaction chamber. During the process, about from 5 to 12% of the mother liquor is continuously removed from the system, this amount also being removed from the mother liquor obtained in batchwise operations.

The yield may be further increased by recycling to the process the washings obtained on washing the moist salt.

The process of the invention is capable of producing very pure salts of the said aminopolycarboxylic acids in yields of up to 95% of theory. Our process is particularly important for the large-scale production of alkali metal salts of aminopolycarboxylic acids, preferably sodium salts of nitrilotriacetic acid, ethylenediaminetetra-acetic acid, hydroxy-

ethethylenediaminotriacetic acid and diethylenetriaminopenta-acetic acid.

By comparison, the yields obtained in previous processes are about 85—88%, and the products obtained may still contain up to 10% of impurities if they are not recrystallized with high losses.

In the following Examples the parts and percentages are by weight unless otherwise stated. The parts by weight relate to the parts by volume as do kilograms to liters.

EXAMPLE 1

50 parts of a sodium nitrilotriacetate solution (38.9% based on the weight of the solution), as obtained from the reaction of sodium cyanide and formaldehyde solution by the method proposed in our earlier Patent Application No. 46435/71 (Serial No. 1358068), are concentrated by evaporation in a heated stirred vessel until about half of the expected theoretical yield of sodium nitrilotriacetate has precipitated. The rate of vaporization is governed by the size and heating capacity of the stirred vessel. The mixture is filtered on a suction filter to give 12.4 parts of moist sodium nitrilotriacetate having a purity of 78.6%. The solid material is washed with a minimum amount of distilled water or water purified by ion exchanger and is then dried to give sodium nitrilotriacetate having a purity of 98.6%. The mother liquor (37 parts containing 39.9% of sodium nitrilotriacetate based on the weight of the mother liquor and having a density of 1.35) is returned to the apparatus used for the preparation of the sodium nitrilotriacetate solution by means of a metering pump. After a steady state has been set up, the flow of material to the first stirred vessel during 24 hours is as follows: 2.095 parts of 34.9% sodium cyanide solution having a density of 1.192, 1.735 parts of 30% formaldehyde solution having a density of 1.086 and 2.758 parts of the mother liquor obtained after separation of sodium nitrilotriacetate. During the same period 9.087 parts of a solution containing 34.4% by weight of sodium nitrilotriacetate leaves the last vessel. The overall yield is 92.7% of theory based on sodium cyanide introduced (17.79 molar parts). The solution is again concentrated so that 47% of the expected theoretical amount of sodium nitrilotriacetate can be separated by filtration. The mother liquor thus obtained (39.8%, density 1.35) is continuously added to the reacting mixture of sodium cyanide and formaldehyde in the manner described above. The amount of material introduced over 24 hours is: 2.940 parts by volume of mother liquor (density 1.35, concentration 39.8%); 2.995 parts by volume of sodium cyanide solution (34.9%, density 1.192) and 2.360 parts by volume of formaldehyde solution (30%, density 1.086). There are obtained 9.076 parts of solution containing

39.4% of sodium nitrilotriacetate. The yield of pure product in this case is 91.8% of theory.

In a comparative test carried out according to our copending Patent Application No. 46435/71 (Serial No. 1358068), the yield was only 86% of theory and the product contained about 9.8% of impurities.

EXAMPLE 2

50 parts of a 43% solution of sodium ethylenediaminetetraacetate (EDTA) as prepared by the process according to our copending Patent Application No. 46435/71, are concentrated by evaporation in a heated stirred vessel until about half of the dissolved salt has precipitated. The precipitate is separated from the mother liquor by centrifuging. There are obtained 10.99 parts of salt having a content of EDTA of 91.1%. If the water is removed from the crystalline product by drying, the salt obtained has a purity of 99.4%.

23.5 parts by volume of the resulting mother liquor containing 20.2% of EDTA and having a density of 1.302 are recycled to the first vessel of the apparatus for preparing the sodium ethylenediaminetetraacetate solution, continuously over 24 hours. During this period, the following materials are also added to the said first vessel: 20.8 parts of a sodium cyanide solution having a sodium cyanide content of 34.1% and a density of 1.195, 2.75 parts of ethylene diamine having a purity of 99%, and a density of 0.900, and 15.7 parts of a 30% formaldehyde solution having a density of 1.086. The material leaving the apparatus during this period is: 58.1 parts by weight of a solution of 35.9% of EDTA. If the weight of the salt which is recycled with the mother liquor is subtracted from the total weight of EDTA produced, the yield is 94.7% based on ethylene diamine introduced. When the mother liquor is not added to the first stirred vessel in the above manner, the same apparatus operating under the same conditions gives yields of only 82% on average.

EXAMPLE 3

50 parts of a 41% solution of sodium hydroxyethylethylenediaminetriacetate (HEDTA) are evaporated in a heated stirred vessel to about half the original volume (if crystallization does not commence automatically, its onset may be accelerated by the addition of a small amount of crystallized HEDTA). The precipitated salt is separated from the mother liquor by centrifuging. There are obtained 11.3 parts of a salt having a content of 88.3% of HEDTA. If the water contained in this product is removed by drying, the salt has a purity of 98.9%.

25 parts by weight of the resulting mother

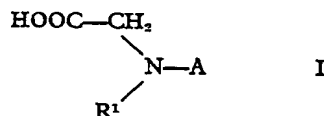
liquor having a content of 23.5% of HEDTA are continuously returned to the apparatus described in Example 1 over 24 hours. During the same period, 11.05 parts by weight of a 34.1% sodium cyanide solution, 7.63 parts by weight of a 30% formaldehyde solution and 2.55 parts by weight of a 99% hydroxyethylethylenediamine are introduced to said first stirred vessel.

- 10 The material leaving the apparatus over 24 hours is 32.1 parts by weight of a solution containing 42.7% of HEDTA. If the amount of salt returned with the mother liquor is subtracted from the total amount produced, the yield is 93.7%. When working under identical conditions but without recycling the mother liquor, the yield is only 84%.

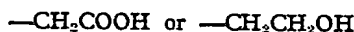
WHAT WE CLAIM IS:—

- 20 1. A process for the manufacture of a pure

alkali metal salt of an aminopolycarboxylic acid of formula I



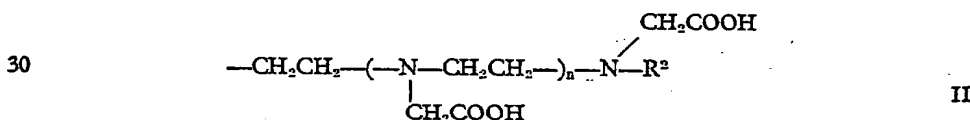
in which R¹ denotes a hydrogen or a group of the formula



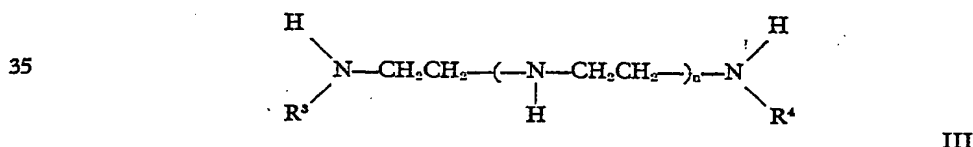
and A denotes a group of the formula



or a group of formula II



where R² has the meaning stated for R¹ in formula I, R¹ and R² being the same or different, and n stands for 0 or an integer from 1 to 5 inclusive, by reacting an alkali metal cyanide, formaldehyde and, where A denotes a group of formula II, a compound of formula III



where R³ and R⁴ are the same or different and denote groups of the formula



- 40 or hydrogen atoms and n has the same meaning as in formula I, in aqueous solution in a reaction chamber and separating the solid alkali metal salt by evaporating the resulting reaction solution, which process includes the improvement of recycling at least part of the reaction solution to the reaction chamber after it has been partially concentrated and freed from the precipitated product salt of the amino polycarboxylic acid.

- 50 2. A process as claimed in claim 1 in which the alkali metal cyanide and formaldehyde are reacted in the absence of a compound of formula III and an alkali metal salt of nitrilotriacetic acid is produced.

- 55 3. A process as claimed in claim 1 in which the alkali metal cyanide and formaldehyde are reacted together with a compound of the formula III and an alkali metal salt of

an aminopolycarboxylic acid in which A denotes a group of formula II is produced.

- 60 4. A process as claimed in claim 3 in which the alkali metal cyanide and formaldehyde are reacted together with ethylene diamine in the reaction chamber and an alkali metal salt of ethylene diamine tetraacetic acid is produced.

- 65 5. A process as claimed in claim 3 in which the alkali metal cyanide and formaldehyde are reacted together with N - hydroxyethyl - ethylene diamine in the reaction chamber and an alkali metal salt of N - hydroxyethyl - ethylene diamine triacetic acid is produced.

- 70 6. A process as claimed in any of claims 1 to 5 in which the reaction solution is evaporated until about 50% of the expected theoretical amount of the salt of the amino polycarboxylic acid has precipitated.

- 75 7. A process as claimed in any of claims 1 to 6, in which the process is carried out in a continuous manner.

- 80 8. A process as claimed in claim 6 or 7

wherein from 5 to 12% of the reaction solution remaining after partial concentration and freeing from the precipitated product is discarded from the system.

- 5 9. A process for the manufacture of pure alkali metal salt of an aminopolycarboxylic acid as claimed in claim 1 and substantially as described in any of the foregoing Examples.
10. Alkali metal salts of aminopolycarboxy-

lic acids whenever prepared by a process as claimed in any of claims 1 to 9. 10

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